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HIRAMATSU KAZUMASA**(54) MANUFACTURE METHOD OF COMPOUND SEMICONDUCTOR SINGLE CRYSTAL AND SINGLE CRYSTAL SUBSTRATE USING SUCH METHOD****(57)Abstract:**

PURPOSE: To provide a method for the manufacture of a III-V nitrogen compound semiconductor single crystal having such a thickness that it is capable of being divided in the direction of thickness for use, and a method for the manufacture of single crystal substrates using such a compound semiconductor single crystal.

CONSTITUTION: A buffer layer is formed on a substrate, and a single crystal of compound semiconductor of a III-group typical element and nitrogen, is grown on the buffer layer by vapor phase epitaxial growth. This method for the manufacture of compound semiconductor single crystals uses a chloride of a III-group typical element and NH₃ for material gas, 1000-1200° C for crystal growth temperature and five hours or longer for crystal growth time. This obtains a single crystal of a compound semiconductor of III-group typical element and nitrogen, having a thickness of 500μm or above in the direction of crystal growth. The obtained single crystal of the compound semiconductor of the III-group typical element and nitrogen, is divided in the direction opposed to that of crystal growth to obtain single crystal substrates.

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CLAIMS

[Claim(s)]

[Claim 1] a substrate top — a buffer layer — forming — this buffer layer top — vapor-phase-epitaxial-growth method the manufacture approach of this compound semiconductor single crystal of growing up the single crystal of the compound semiconductor of an III group typical element and nitrogen — it is — material gas — ** The chloride of an III group typical element, and NH₃ ** — the manufacture approach of the compound semiconductor single crystal characterized by carrying out, making crystal growth temperature into 1000 degrees C - 1200 degrees C, and making crystal growth time amount into 5 hours or more.

[Claim 2] The manufacture approach of a compound semiconductor single crystal according to claim 1 that the compound semiconductor of an III group typical element and nitrogen is GaN, and the chloride of this III group typical element is GaCl.

[Claim 3] The manufacture approach of a compound semiconductor single crystal according to claim 1 that a substrate is a sapphire crystal substrate.

[Claim 4] a vapor-phase-epitaxial-growth method — HVPE — law and MOVPE — law or MBE — the manufacture approach of the compound semiconductor single crystal according to claim 1 which is law.

[Claim 5] It has the thickness of 500 micrometers or more in the crystal growth direction. Single crystal of the compound semiconductor of an III group typical element and nitrogen.

[Claim 6] The GaN single crystal which has the thickness of 1mm or more in the crystal growth direction.

[Claim 7] The manufacture approach of the single crystal substrate characterized by countering in the crystal growth direction and dividing a single crystal according to claim 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] To this compound semiconductor single crystal and pan which are obtained by the ingredient of a light emitting device etc. by the manufacture approach of a useful compound semiconductor single crystal, and its manufacture approach, this compound semiconductor single crystal in detail this invention about the manufacture approach of the single crystal substrate from this compound semiconductor single crystal It is related with what is the compound semiconductor of an III group typical element and nitrogen.

[0002]

[Description of the Prior Art] The compound semiconductor which consists of an III group's typical element and nitrogen is known as a semiconductor material useful to a light emitting device etc. from 2 yuan things, AlN, GaN, etc., to pluralism things, such as InAlBN, InGaBN, InGaAlN, InGaAlBN, etc. which are the mixed crystal of such arbitration. (the followings and these compound semiconductors, i.e., the 2 yuan compound semiconductor of an III group typical element and nitrogen, — and — among these — since — the compound semiconductor single crystal of the plural mixed crystal with which it comes to choose one or more things is called "an III-V group's nitrogen system compound single crystal".) For example, the above Since the typical GaN single crystal of an III-V group's nitrogen system compound single crystal has direct transition mold band structure, possible [efficient luminescence], since the band gap in a room temperature is as large as about 3.4eV, it produces blue - ultraviolet luminescence, and is a suitable ingredient for the demand of a semiconductor device. However, since [that this GaN system single crystal has high crystal growth temperature and] the balanced dissociation pressure of the nitrogen near crystal growth temperature is high, it is very difficult to grow up a bulk single crystal from melt.

[0003] On the other hand, as an approach of growing up the single crystal of GaN, ZnO was formed as a buffer layer on silicon on sapphire, the method of growing up a GaN single crystal on it was proposed, and the quality of a GaN single crystal thin film improved by adoption of this approach in recent years.

[0004]

[Problem(s) to be Solved by the Invention] However, the grid mismatching of GaN and ZnO still exists also by the above-mentioned approach. For this reason, the GaN single crystal obtained had the problem of being easy to damage having a defect on structure, and a mechanical strength being weak since the thickness of the growth direction is not enough, and a crack occurring in a GaN single crystal side moreover at the time of cooling after single crystal growth since the difference of the coefficient of thermal expansion by the side of a substrate is large etc. Therefore, in the conventional growth, even if it grew up the GaN single crystal of the shape of a wafer of about 300-micrometer thickness on the silicon on sapphire of several cm angle, while cooling to the room temperature, the crack arose, and even if large, only the GaN single crystal of the small area of 5x5mm angle extent was obtained. So, the above-mentioned problem will become remarkable as it large-area-izes a GaN single crystal, and it is a very serious problem.

[0005] The single crystal which the purpose of this invention can avoid the breakage after growth also to not only a GaN single crystal but an III-V group's nitrogen system compound single crystal, and is obtained being able to use as an independent substrate is offering the manufacture approach of this single crystal that is so thick that it divides in the thickness direction and two or more independent substrates are obtained from the first. Other purposes of this invention have the thickness of 500 micrometers or more in the crystal growth direction. It is offering an III-V group's nitrogen system compound single crystal, and the GaN single crystal which has the thickness of 500 micrometers or more in the crystal growth direction especially.

[0006]

[Means for Solving the Problem] by the way, it sets under a Prior-art level — there being no need according to rank which grows up an III-V group's nitrogen system compound single crystal, especially GaN single crystal in the crystal growth direction on a large scale, and having various problems, such as breakage at the time of crystal growth, as further above-mentioned — conjointly — the enlargement to the crystal growth direction of an III-V group's nitrogen system compound single crystal — an attempt — the actual condition is that there was no motive according to rank made like. therefore, the stress which it is an III-V group's nitrogen system compound single crystal, and the good thing to which the thickness of the crystal growth direction exceeds 500 micrometers does not exist conventionally, and originates in the coefficient-of-thermal-expansion difference at the time of cooling by the conventional thickness — a GaN single crystal — damaging — very much — small — only the area thing was able to be obtained. the bottom of this situation — setting — this invention persons — for the first time — being concerned — thick dividing the nitrogen system compound single crystal of the thick III-V group who invents an III-V group's good nitrogen system compound single crystal, and establishes the manufacture

approach, and starts further — a crystal substrate — the yield — good — it can manufacture — in addition — and it found out that the crystal substrate of the large area of extent which was not able to be manufactured until now could be manufactured. Namely, this invention persons specify a vapor-phase-epitaxial-growth method out of the various crystal growth approaches, and are ** about material gas. It is ** by considering as the combination of the chloride of an III group typical element, and NH₃, and specifying crystal growth temperature and crystal growth time amount. It succeeded in growing up an III-V group's nitrogen system compound single crystal on a large scale.

[0007] This invention has the following descriptions.

(1) a substrate top — a buffer layer — forming — this buffer layer top — vapor-phase-epitaxial-growth method the manufacture approach of this compound semiconductor single crystal of growing up the single crystal of the compound semiconductor of an III group typical element and nitrogen — it is — material gas — ** The chloride of an III group typical element, and NH₃ ** — the manufacture approach of the compound semiconductor single crystal characterized by carrying out, making crystal growth temperature into 1000 degrees C - 1200 degrees C, and making crystal growth time amount into 5 hours or more.

(2) The compound semiconductor of an III group typical element and nitrogen is GaN, and it is **. The manufacture approach of a compound semiconductor single crystal given in (1) that the chloride of an III group typical element is GaCl.

(3) The manufacture approach of a compound semiconductor single crystal given in (1) that a substrate is a sapphire crystal substrate.

(4) a vapor-phase-epitaxial-growth method — HVPE — law and MOVPE — law or MBE — the manufacture approach of the compound semiconductor single crystal given in (1) which is law.

Moreover, the compound semiconductor single crystal obtained by the manufacture approach of this invention has the following descriptions.

(5) It has the thickness of 500 micrometers or more in the crystal growth direction. Single crystal of the compound semiconductor of an III group typical element and nitrogen.

(6) The GaN single crystal which has the thickness of 500 micrometers or more in the crystal growth direction.

(7) The manufacture approach of the single crystal substrate by countering in the crystal growth direction and dividing the single crystal of the above-mentioned (5) publication.

[0008] Hereafter, based on a drawing, this invention is explained more to a detail. Drawing 1 is this invention. It is the mimetic diagram showing the manufacture approach of an III-V group's nitrogen system compound single crystal. This invention The manufacture approach of an III-V group's nitrogen system compound single crystal After growing up the buffer layer 2 which consists of matter with good grid adjustment with an III-V group's nitrogen system compound single crystal on this drawing (a) substrate 1. On the this (drawing b) this buffer layer 2, it is the purpose by the vapor-phase-epitaxial-growth method. It is the manufacture approach of having the process into which an III-V group's nitrogen system compound single crystal 3 is grown up. Material gas at the time of the epitaxial growth The chloride of an III group typical element, and NH₃ By carrying out and specifying the optimum value of crystal growth temperature and crystal growth time amount further In the former, it is fully so thick that it was not obtained. It makes it possible to obtain an III-V group's nitrogen system compound single crystal 3. Furthermore, as shown in this drawing (c), this single crystal 3 obtained if needed is separated from a substrate side, and it is good also as an independent single crystal substrate.

[0009] As an ingredient of the above-mentioned substrate 1, it is the manufacture purpose. The grid adjustment over an III-V group's nitrogen system compound single crystal 3 is good, and the thermal resistance to the growth temperature moreover specified in this invention should be just good. That in which the lattice constant of the a-axis in a crystal lattice also usually has the crystal structure of the Ur Die Zeit mold which is less than **5% above all less than **20% to it of an III-V group's nitrogen system compound single crystal as matter with good grid adjustment to an III-V group's nitrogen system compound single crystal is desirable. As such an ingredient, a sapphire crystal substrate, a ZnO substrate, a SiC substrate, etc. are illustrated, and it is the manufacture purpose by the conventional crystal grown method on these substrates further. The substrate which comes to carry out thin film growth of the same thing as an III-V group's nitrogen system compound through direct or a buffer layer is illustrated. Also in these substrates, a sapphire crystal substrate and a ZnO substrate have the crystal structure of GaN, and since a lattice constant is also near, they are desirable especially for the manufacture approach of this invention.

[0010] The shape of surface type of a substrate is the manufacture purpose as it is. Although it becomes the shape of surface type of an III-V group's nitrogen system compound single crystal in many cases, even if it uses the substrate of a large area by this invention, it is fully thick without breakage. Since an III-V group's nitrogen system compound single crystal can grow, the shape of surface type of a substrate can also use a 5cmx5cm rectangle or the thing beyond it.

[0011] The ingredient used for the above-mentioned buffer layer is the manufacture purpose. Just good [the grid adjustment over an III-V group's nitrogen system compound single crystal 3], ZnO, BeO, HgO(s), or these compounds are mentioned, and it is the purpose out of these. What is necessary is to choose as the lattice constant of an III-V group's nitrogen system compound single crystal what is adjusted most, or to determine a presentation ratio, and just to use. Also in the above-mentioned ingredient, the etching removal nature of ZnO by the acid is good, and it is the manufacture purpose. It is suitable as matter which uses an III-V group's nitrogen system compound single crystal for a buffer layer also from the point separated independently. Although the thickness of a buffer layer 2 is not limited, 0.02-2 micrometers of 0.01 micrometers - 2 micrometers of crystallinity of a single crystal to grow up on a buffer layer will usually become good by being most preferably referred to as about 0.02-1.5 micrometers preferably.

[0012] the formation approach of a buffer layer 2 — MOVPE — law (Metal Organic Vapor Phase Epitaxy : organic metal vapor-phase-epitaxial-growth method) — The HVPE method (Hydride VPE : hydride vapor-phase-epitaxial-growth method), LPE — law (liquid phase epitaxy) and MBE — law (Molecular Beam Epitaxy: molecular beam epitaxy) — The

forming-membranes methods, such as a spatter besides epitaxial grown methods, such as the GS-MBE method (gas source MBE law) and the CBE method (chemical beam epitaxial grown method), and a CVD method, are mentioned as an effective approach. Since especially the MOVPE method can form the film which is a non-equilibrium state and has a certain amount of thickness, it is suitable for formation of a buffer layer 2. Moreover, formation of a buffer layer 2 and the purpose It is from a buffer layer 2 only at changing supply of an ingredient, if formation of an III-V group's nitrogen system compound single crystal 3 is performed using the same epitaxial growth approach. Continuous growth on the spot is attained to an III-V group's nitrogen system compound single crystal.

[0013] it is the manufacture purpose an III-V group's nitrogen system compound single crystal 3 — said — as [carried out] — they are the compound semiconductors of the plural mixed crystal which consists of one or more thing in the 2 yuan compound semiconductors (BN, AlN, GaN, InN, etc.) which consist of an III group's typical element and nitrogen, and these 2 yuan compound semiconductor (AlBN, GaBN, GaAlN, InBN, InAlN, InGaN, GaAlBN, InAlBN, InGaBN, InGaAlN, etc.). These Also in an III-V group's nitrogen system compound single crystal, the most useful thing is a GaN single crystal in this invention.

[0014] Let this invention be the purpose. It has the description important for the growth conditions at the time of growing up an III-V group's nitrogen system compound single crystal 3 by the vapor-phase-epitaxial-growth method. as the vapor-phase-epitaxial-growth method for growing up an III-V group's nitrogen system compound single crystal 3 — HVPE — law and MBE — law and MOVPE — law and LPE — law and GS-MBE — although law and the CBE method are illustrated — desirable — HVPE — law and MBE — law and MOVPE — it is law and crystallinity is good especially from the point that an III-V group's nitrogen system compound single crystal 3 can be grown up at high speed — especially — HVPE — law is a desirable approach.

[0015] As material gas, it corresponds to the presentation of an III-V group's nitrogen system compound. The chlorides (BCl, GaCl, InCl, etc.) of an III group typical element, and NH₃ What was combined is used. For example, in growth of a GaN single crystal, it is GaCl and NH₃. In growth of an InN system single crystal, it is combination InCl and NH₃ The gas which consists of combination is used.

[0016] It becomes possible by making preferably 1000 degrees C - 1200 degrees C of crystal growth temperature into 1050 degrees C - 1150 degrees C to grow up the target single crystal sufficiently thickly. At less than 1000 degrees C, the problem polycrystal-ized, without being single-crystal-ized arises, and when higher than 1200 degrees C, there is an inclination which is [single-crystal-] hard to beized.

[0017] The thickness of the request beyond 5cm or it can be obtained as the so-called bulk crystal by it being referred to as 500 micrometers or more which was not able to obtain thickness of the crystal growth direction at all by the former, and continuing growth further, if crystal growth time amount is 5 hours or more. A crack may occur in a GaN single crystal side in less than 5 hours at the time of cooling after a reason without sufficient thickness as a bulk crystal, and single crystal growth.

[0018] As mentioned above, the bulk single crystal of an III-V group's nitrogen system compound single crystal is obtained by the manufacture approach of this invention. By separating this from a substrate and a buffer layer, it becomes possible to obtain the independent substrate of this single crystal. Furthermore, depending on the thickness of the this single crystal made to separate, this can be further divided in the thickness direction, and it can consider as the independent substrate of this single crystal. As shown in drawing 1 (c), etching etc. removes a buffer layer 2, or in this part, it cuts mechanically and describes above. An III-V group's nitrogen system compound single crystal 3 is separated, and further, if it is enough like the thickness of the single crystal 3 made to this separate amounts to 10mm, it can divide this in the thickness direction further, and can consider as the independent substrate of this single crystal. What is necessary is just to perform the division concerned by the approach of the very thing known.

[0019]

[Function] According to the manufacture approach of the above-mentioned compound semiconductor single crystal, generating and breakage of a crack can be avoided now at the time of cooling after single crystal growth of an III-V group's nitrogen system compound. Moreover, this invention The bulk single crystal of an III-V group's nitrogen system compound has the thickness of 1mm or more, if enough like the thickness amounts to 10mm, can divide this in the thickness direction further, and can mass-produce the independent substrate of this single crystal easily.

[0020]

[Example] Hereafter, an example is shown and this invention is explained concretely.

Example 1 this example shows the example of manufacture of the GaN single crystal independent substrate which divides the bulk single crystal of GaN, and this further, and is obtained. the 100nm buffer layer which consists of ZnO by the spatter on 5cmx5cm and silicon on sapphire with a thickness of 300 micrometers — forming — this buffer layer top — receiving — HVPE — the GaN single crystal was grown up by law. It is material gas to supply GaCl and NH₃ When it carried out, epitaxial growth was carried out where growth temperature is maintained at 1100**50 degrees C, and growth time amount was made into 300 hours, the 30mm GaN single crystal grew in the growth direction. Subsequently, etching removal of the ZnO of a buffer layer was carried out, the above-mentioned GaN single crystal was separated from the substrate side, and the crystal lump GaN single crystal independent [huge] which cannot get was obtained in the former of 30mm in 5cmx5cm and thickness. Cutting division of the GaN single crystal obtained above was carried out in the thickness direction using the diamond scribe, and several many substrates 5cmx5cm and GaN single crystal independent [with a thickness of 300 micrometers] were obtained.

[0021] In example 2 example 1, when growth time amount was made into 10 hours (example 2), 50 hours (example 3), and 100 hours (example 4), respectively, the GaN single crystal (1mm (example 2), 5mm (example 3), and 10mm (example 4)) grew in the growth direction respectively. Subsequently, etching removal of the ZnO of a buffer layer was carried out, the

above-mentioned GaN single crystal was separated from the substrate side, and the crystal lump GaN single crystal independent [huge] was obtained.

[0022] The ingredient which forms a buffer layer is set to ZnO in example 5 example 1, and it is material gas InCl and NH₃. The InN bulk single crystal was similarly produced except [all] having carried out. The 1mm InN single crystal grew in the growth direction in this way. Subsequently, etching removal of the ZnO of a buffer layer was carried out, the above-mentioned InN single crystal was separated from the substrate side, and the crystal lump 3cmx3cm and InN single crystal independent [with a thickness of 1mm] was obtained.

[0023]

[Effect of the Invention] It is this invention as explained in full detail above. By the manufacture approach of an III-V group's nitrogen system compound single crystal, generating and breakage of the crack of this single crystal can be avoided, and it has the thickness of 500 micrometers or more in the crystal growth direction. An III-V group's nitrogen system compound single crystal is obtained. By separating this single crystal from a substrate, it was not obtained by the former. An III-V group's nitrogen system compound, especially the bulk single crystal of GaN are obtained. Furthermore, it is **. Though it is a large area like 50mmx50mm, since the bulk single crystal of an III-V group's nitrogen system compound will be able to become so large-sized that it amounts also to 50mm, it divides the thickness of the crystal growth direction with the thickness of a request of this in the crystal growth direction, and becomes possible [obtaining a single crystal independent substrate].

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the type section Fig. showing an example of the manufacture approach of an III group's nitrogen system compound single crystal.

[Description of Notations]

1 Substrate

2 Buffer Layer

3 Single Crystal of III Group's Nitrogen System Compound

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最終頁に続く

(54)【発明の名称】 化合物半導体単結晶の製造方法、該化合物半導体の単結晶および単結晶基板の製造方法

(57)【要約】

【目的】 III-V族の窒素系化合物単結晶であって、厚み方向に分割して使用しえるほど肉厚のものを製造しえる化合物半導体単結晶の製造方法、500 μ m以上の厚みを有する化合物半導体の単結晶および該単結晶を使用する単結晶基板の製造方法を提供すること。

【構成】 基板上にバッファ層を形成し該バッファ層上に気相エピタキシャル成長法によって III族典型元素と窒素との化合物半導体の単結晶を成長させる該化合物半導体単結晶の製造方法であって、原料ガスを該 III族典型元素の塩化物とNH₃とし、結晶成長温度を1000℃~1200℃とし、結晶成長時間を5時間以上とすることによる化合物半導体単結晶の製造方法。上記方法にて得ることのできる結晶成長方向に500 μ m以上の厚みを有する III族典型元素と窒素との化合物半導体の単結晶。該 III族典型元素と窒素との化合物半導体の単結晶を結晶成長方向に対向して分割することによる単結晶基板の製造方法。

【特許請求の範囲】

【請求項1】 基板上にバッファ層を形成し該バッファ層上に気相エピタキシャル成長法によって III族典型元素と窒素との化合物半導体の単結晶を成長させる該化合物半導体単結晶の製造方法であって、原料ガスを該 III族典型元素の塩化物と NH_3 とし、結晶成長温度を $1000^\circ\text{C} \sim 1200^\circ\text{C}$ とし、結晶成長時間を5時間以上とすることを特徴とする化合物半導体単結晶の製造方法。

【請求項2】 III族典型元素と窒素との化合物半導体が GaN であり、該III族典型元素の塩化物が GaCl である請求項1記載の化合物半導体単結晶の製造方法。

【請求項3】 基板が、サファイア結晶基板である請求項1記載の化合物半導体単結晶の製造方法。

【請求項4】 気相エピタキシャル成長法が、HVPE法、MOVPE法、又はMBE法である請求項1記載の化合物半導体単結晶の製造方法。

【請求項5】 結晶成長方向に $500\mu\text{m}$ 以上の厚みを有する III族典型元素と窒素との化合物半導体の単結晶。

【請求項6】 結晶成長方向に 1mm 以上の厚みを有する GaN 単結晶。

【請求項7】 請求項5記載の単結晶を、結晶成長方向に対向して分割することを特徴とする単結晶基板の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、発光素子の材料等に有用な化合物半導体単結晶の製造方法およびその製造方法によって得られる該化合物半導体単結晶、さらには該化合物半導体単結晶からの単結晶基板の製造方法に関し、詳しくは、該化合物半導体単結晶が III族典型元素と窒素との化合物半導体であるものに関する。

【0002】

【従来の技術】III族の典型元素と窒素とからなる化合物半導体は、例えば AlN や GaN 等の2元のものから、これらの任意の混晶である InAlBN 、 InGaBN 、 InGaAlN 、 InGaAlBN 等の多元のものまで、発光素子等に有用な半導体材料として知られている。(以下、これらの化合物半導体、即ち、III族典型元素と窒素との2元の化合物半導体および、これらのうちから1以上のものが選択されてなる多元混晶の化合物半導体単結晶を「III-V族の窒素系化合物単結晶」という。)

例えば、上記 III-V族の窒素系化合物単結晶の代表的なものである GaN 単結晶は、直接遷移型バンド構造を有するため、高効率の発光が可能であり、かつ、室温でのバンドギャップが約 3.4eV と大きいため青色～紫外発光を生じ、半導体デバイスの要求に好適な材料である。しかし、この GaN 系単結晶は、結晶成長温度が高く、また、結晶成長温度付近での窒素の平衡解離圧が高

いため、融液からバルク単結晶を成長させることは極めて困難である。

【0003】これに対して、近年、 GaN の単結晶を成長させる方法として、サファイア基板上に ZnO をバッファ層として成膜し、その上に GaN 単結晶を成長させる方法が提案され、この方法の採用によって GaN 単結晶薄膜の品質は向上した。

【0004】

【発明が解決しようとする課題】ところが、上記方法によっても、 GaN と ZnO との格子不整合は未だ存在する。このため得られる GaN 単結晶は構造上の欠陥を有し、また、成長方向の厚みが十分でないため機械的強度が弱く、しかも、基板側との熱膨張係数の差が大きいため、単結晶成長後の冷却時において GaN 単結晶側にクラックが発生する等、破損し易いという問題があった。そのため、従来の成長において、数 cm 角のサファイア基板上におよそ $300\mu\text{m}$ 厚さのウエハー状の GaN 単結晶を成長させても、室温まで冷却する間にクラックが生じ、大きくても $5 \times 5\text{mm}$ 角程度の小面積の GaN 単結晶しか得られなかった。それ故に、上記問題は GaN 単結晶を大面積化するにしがたい顕著なものとなり、非常に深刻な問題である。

【0005】本発明の目的は、 GaN 単結晶だけでなく、III-V族の窒素系化合物単結晶に対しても、成長後の破損を回避でき、得られる単結晶が単独の基板として用い得ることはもとより、厚み方向に分割し複数枚の単独の基板が得られるほど厚いものであるような該単結晶の製造方法を提供することである。本発明の他の目的は、結晶成長方向に $500\mu\text{m}$ 以上の厚みを有する III-V族の窒素系化合物単結晶、特に、結晶成長方向に $500\mu\text{m}$ 以上の厚みを有する GaN 単結晶を提供することである。

【0006】

【課題を解決するための手段】ところで、従来の技術水準下においては、III-V族の窒素系化合物単結晶、特に GaN 単結晶を、結晶成長方向へ大型に成長させる格別の必要性がなく、さらに上記の通り結晶成長時の破損等の種々の問題を有することが相まって、III-V族の窒素系化合物単結晶の結晶成長方向への大型化を試みようとする格別の動機はなかったのが実情である。従って、III-V族の窒素系化合物単結晶であって、結晶成長方向の厚みが $500\mu\text{m}$ を越える良質のものは従来存在せず、また、従来の厚みでは冷却時の熱膨張係数差に起因する応力により GaN 単結晶は破損し、非常に小面積なものしか得ることができなかった。かかる状況下において、本発明者らは、初めて当該肉厚の III-V族の良質な窒素系化合物単結晶を創製し、且つその製造方法を確立し、さらにかかる肉厚の III-V族の窒素系化合物単結晶を分割することによって、結晶基板を歩留りよく製造でき、尚且つ、これまで製造できなかった程度の

大面積の結晶基板が製造できることを見出した。即ち、本発明者らは種々の結晶成長方法の中から、気相エピタキシャル成長法を特定し、原料ガスを該 III 族典型元素の塩化物と NH_3 との組み合わせとし、結晶成長温度および結晶成長時間を特定することによって、該 III-V 族の窒素系化合物単結晶を大型に成長させることに成功した。

【0007】本発明は以下の特徴を有するものである。

(1) 基板の上にバッファ層を形成し該バッファ層上に気相エピタキシャル成長法によって III 族典型元素と窒素との化合物半導体の単結晶を成長させる該化合物半導体単結晶の製造方法であって、原料ガスを該 III 族典型元素の塩化物と NH_3 とし、結晶成長温度を $1000^\circ\text{C} \sim 1200^\circ\text{C}$ とし、結晶成長時間を 5 時間以上とすることを特徴とする化合物半導体単結晶の製造方法。

(2) III 族典型元素と窒素との化合物半導体が GaN であり、該 III 族典型元素の塩化物が GaCl である

(1) 記載の化合物半導体単結晶の製造方法。

(3) 基板が、サファイア結晶基板である (1) 記載の化合物半導体単結晶の製造方法。

(4) 気相エピタキシャル成長法が、HVPE 法、MOVPE 法、又は MBE 法である (1) 記載の化合物半導体単結晶の製造方法。

また、本発明の製造方法によって得られる化合物半導体単結晶は以下の特徴を有するものである。

(5) 結晶成長方向に $500 \mu\text{m}$ 以上の厚みを有する III 族典型元素と窒素との化合物半導体の単結晶。

(6) 結晶成長方向に $500 \mu\text{m}$ 以上の厚みを有する GaN 単結晶。

(7) 上記 (5) 記載の単結晶を、結晶成長方向に対向して分割することによる単結晶基板の製造方法。

【0008】以下、図面に基づき本発明をより詳細に説明する。図 1 は、本発明の III-V 族の窒素系化合物単結晶の製造方法を示す模式図である。本発明の III-V 族の窒素系化合物単結晶の製造方法は、同図 (a) 基板 1 上に、III-V 族の窒素系化合物単結晶との格子整合性の良好な物質からなるバッファ層 2 を成長させた後、同図 (b) 該バッファ層 2 上に、気相エピタキシャル成長法によって目的の III-V 族の窒素系化合物単結晶 3 を成長させる工程を有する製造方法であって、そのエピタキシャル成長時の原料ガスを III 族典型元素の塩化物と NH_3 とし、さらに結晶成長温度と結晶成長時間の最適値を特定することによって、従来では得られなかった程十分に厚い III-V 族の窒素系化合物単結晶 3 を得ることを可能とするものである。またさらに、同図 (c) に示すように、必要に応じて得られた該単結晶 3 を基板側から分離し単独の単結晶基板としてもよい。

【0009】上記基板 1 の材料としては、製造目的の III-V 族の窒素系化合物単結晶 3 に対する格子整合性が良好で、しかも、本発明において特定される成長温度に

対する耐熱性が良好なものであればよい。III-V 族の窒素系化合物単結晶に対する格子整合性の良好な物質としては、結晶格子における a 軸の格子定数が、III-V 族の窒素系化合物単結晶のそれに対して、通常 $\pm 20\%$ 以内、就中 $\pm 5\%$ 以内であるウルツァイト型の結晶構造も持つものが好ましい。このような材料としては、サファイア結晶基板、 ZnO 基板、 SiC 基板等が例示され、さらにはこれらの基板上に、従来の結晶成長法によって製造目的の III-V 族の窒素系化合物と同じものを直接またはバッファ層を介して薄膜成長させてなる基板等が例示される。これらの基板のなかでも、サファイア結晶基板、 ZnO 基板は、 GaN の結晶構造を持ち、格子定数も近いので、本発明の製造方法にとって特に好ましい。

【0010】基板の表面形状は、そのまま、製造目的である III-V 族の窒素系化合物単結晶の表面形状となる場合が多いが、本発明によって大面積の基板を用いても、破損なく十分に厚い III-V 族の窒素系化合物単結晶が成長可能であるため、基板の表面形状も、 $5 \text{ cm} \times 5 \text{ cm}$ の方形、またはそれ以上のものを用いることが可能である。

【0011】上記バッファ層に用いられる材料は、製造目的の III-V 族の窒素系化合物単結晶 3 に対する格子整合性が良好なものであればよく、 ZnO 、 BeO 、 HgO 、またはこれらの化合物等が挙げられ、これらの中から、目的の III-V 族の窒素系化合物単結晶の格子定数に最も整合するものを選択し、または組成比を決定して用いればよい。上記材料のなかでも、 ZnO は、酸によるエッチング除去性が良好であり、製造目的の III-V 族の窒素系化合物単結晶を単独に分離する点からも、バッファ層に用いる物質として好適である。バッファ層 2 の厚みは限定されるものではないが、通常、 $0.01 \mu\text{m} \sim 2 \mu\text{m}$ 、好ましくは $0.02 \sim 2 \mu\text{m}$ 、最も好ましくは $0.02 \sim 1.5 \mu\text{m}$ 程度とすることによって、バッファ層上に成長する目的の単結晶の結晶性は良質なものとなる。

【0012】バッファ層 2 の形成方法は、MOVPE 法 (Metal Organic Vapor Phase Epitaxy : 有機金属気相エピタキシャル成長法)、HVPE 法 (Hydride VPE : ハイドライド気相エピタキシャル成長法)、LPE 法 (液相エピタキシャル成長法)、MBE 法 (Molecular Beam Epitaxy : 分子線エピタキシャル成長法)、GS-MBE 法 (ガスソース MBE 法)、CBE 法 (ケミカルビームエピタキシャル成長法) 等のエピタキシャル成長法その他、スパッタ法、CVD 法等の成膜法が有効な方法として挙げられる。特に、MOVPE 法は非平衡状態で、且つある程度の厚みを有する膜を形成可能であるため、バッファ層 2 の形成には好適である。また、バッファ層 2 の形成と目的の III-V 族の窒素系化合物単結晶 3 の形成とを、同じエピタキシャル成長法を用いて行

なえば、材料の供給を変えるだけでバッファ層2からⅡ-Ⅴ族の窒素系化合物単結晶へと、その場での連続的な成長が可能となる。

【0013】製造目的であるⅢ-Ⅴ族の窒素系化合物単結晶3は、前記したように、Ⅲ族の典型元素と窒素とからなる2元の化合物半導体(BN、AlN、GaN、InN等)、およびこれら2元の化合物半導体のうちの1以上のものからなる多元混晶の化合物半導体(AlBN、GaBN、GaAlN、InBN、InAlN、InGaN、GaAlBN、InAlBN、InGaBN、InGaAlN、InGaAlBN等)である。これらⅢ-Ⅴ族の窒素系化合物単結晶の中でも、本発明において最も有用なものはGaN単結晶である。

【0014】本発明は、目的とするⅢ-Ⅴ族の窒素系化合物単結晶3を気相エピタキシャル成長法によって成長させる際の成長条件に重要な特徴を有する。Ⅲ-Ⅴ族の窒素系化合物単結晶3を成長させる気相エピタキシャル成長法としては、HVPE法、MBE法、MOVPE法、LPE法、GS-MBE法、CBE法が例示されるが、好ましくはHVPE法、MBE法、MOVPE法であり、なかでも結晶性の良好なⅢ-Ⅴ族の窒素系化合物単結晶3を高速で成長できる点から特にHVPE法が好ましい方法である。

【0015】原料ガスとしては、Ⅲ-Ⅴ族の窒素系化合物の組成に対応するⅢ族典型元素の塩化物(BCl、GaCl、InCl等)とNH₃を組み合わせたものを使用する。例えば、GaN単結晶の成長にはGaClとNH₃との組み合わせを、InN系単結晶の成長にはInClとNH₃との組み合わせよりなるガスを用いる。

【0016】結晶成長温度を、1000℃~1200℃、好ましくは1050℃~1150℃とすることによって、目的の単結晶を充分厚く成長させることが可能となる。1000℃未満では、単結晶化されずに多結晶化される問題が生じ、1200℃よりも高いと、単結晶化されにくい傾向がある。

【0017】結晶成長時間は、5時間以上であれば、結晶成長方向の厚みを、従来では全く得られなかった500μm以上とすることができ、さらに成長を継続することで、所謂バルク結晶として5cmあるいはそれ以上の所望の厚みを得ることができる。5時間未満では、バルク結晶としての十分な厚さがなく、単結晶成長後の冷却時において、GaN単結晶側にクラックが発生することがある。

【0018】上記のように、本発明の製造方法によって、Ⅲ-Ⅴ族の窒素系化合物単結晶のバルク単結晶が得られる。これを基板およびバッファ層から分離することによって、該単結晶の単独基板を得ることが可能となる。さらには、該分離させた単結晶の厚みによっては、これをさらに厚み方向に分割し該単結晶の単独基板とす

ることができる。図1(c)に示すように、バッファ層2をエッチング等によって除去するか、この部分で機械的に切断し、上記Ⅲ-Ⅴ族の窒素系化合物単結晶3を分離し、さらには、該分離させた単結晶3の厚みが、例えば10mmに達するほどの充分なものであれば、これをさらに厚み方向に分割し該単結晶の単独基板とすることができる。当該分割は自体既知の方法によって行えばよい。

【0019】

【作用】上記化合物半導体単結晶の製造方法によれば、Ⅲ-Ⅴ族の窒素系化合物の単結晶成長後の冷却時に、クラックの発生や破損を回避できるようになる。また、本発明のⅢ-Ⅴ族の窒素系化合物のバルク単結晶は1mm以上の厚みを有し、その厚みが、例えば10mmに達するほどの充分なものであれば、これをさらに厚み方向に分割し、該単結晶の単独基板を容易に量産することができる。

【0020】

【実施例】以下、実施例を示し本発明を具体的に説明する。

実施例1

本実施例では、GaNのバルク単結晶およびこれをさらに分割して得られるGaN単結晶単独の基板の製造例を示す。5cm×5cm、厚さ300μmのサファイア基板上に、スパッタ法によってZnOよりなる100nmのバッファ層を形成し、このバッファ層上に対して、HVPE法によってGaN単結晶を成長させた。供給する原料ガスをGaClとNH₃とし、成長温度を1100±50℃に維持した状態でエピタキシャル成長させ、成長時間を300時間としたところ成長方向に30mmのGaN単結晶が成長した。ついでバッファ層のZnOをエッチング除去し、基板側から上記GaN単結晶を分離して、5cm×5cm、厚さ30mmという従来では得ることのできない巨大なGaN単結晶単独の結晶塊を得た。上記で得られたGaN単結晶をダイヤモンド・スクライパーを用いて厚み方向に切断分割し、5cm×5cm、厚さ300μmのGaN単結晶単独の基板が多数枚得られた。

【0021】実施例2

実施例1において、成長時間を、それぞれ10時間(実施例2)、50時間(実施例3)、100時間(実施例4)としたところ、各々成長方向に1mm(実施例2)、5mm(実施例3)、10mm(実施例4)のGaN単結晶が成長した。ついでバッファ層のZnOをエッチング除去し、基板側から上記GaN単結晶を分離して、巨大なGaN単結晶単独の結晶塊を得た。

【0022】実施例5

実施例1において、バッファ層を形成する材料をZnOとし、原料ガスをInClとNH₃とした以外は全て同様にしてInNバルク単結晶を作製した。かくして成長

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方向に1mmのInN単結晶が成長した。ついでバッファ層のZnOをエッチング除去し、基板側から上記InN単結晶を分離して、3cm×3cm、厚さ1mmのInN単結晶単独の結晶塊を得た。

【0023】

【発明の効果】以上詳述したように、本発明のIII-V族の窒素系化合物単結晶の製造方法によって、該単結晶のクラックの発生および破損が回避でき、結晶成長方向に500μm以上の厚みを有するIII-V族の窒素系化合物単結晶が得られる。この単結晶を基板から分離することによって、従来では得られなかったIII-V族の窒素系化合物、特にGaNのバルク単結晶が得られる。さ

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らに該III-V族の窒素系化合物のバルク単結晶は、50mm×50mm程の面積でありながら、その結晶成長方向の厚みを50mmにも達するほど大型のものとなり得るため、これを結晶成長方向に所望の厚みをもって分割し、単結晶単独の基板を得ることが可能となる。

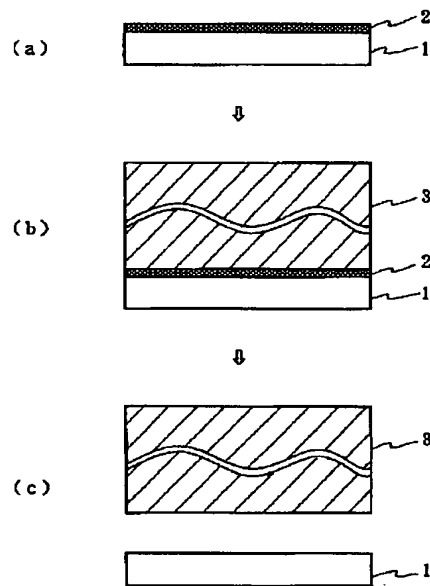
【図面の簡単な説明】

【図1】III族の窒素系化合物単結晶の製造方法の一例を示す模式断面図である。

【符号の説明】

- | | |
|---|-----------------|
| 1 | 基板 |
| 2 | バッファ層 |
| 3 | III族の窒素系化合物の単結晶 |

【図1】



フロントページの続き

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